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Thermal Quenching Mechanism of $\text{CaAlSiN}_3\text{:Eu}^{2+}$ Red Phosphor

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Abstract

$\text{CaAlSiN}_3\text{:Eu}^{2+}$ is a widely applied phosphor in white LEDs (w-LEDs) because of strong blue absorption and efficient red luminescence. The good stability against thermal quenching has been well established, but the mechanism for the luminescence quenching at high temperatures has not been elucidated yet. In this report, we investigate the possibility of thermal ionization quenching by thermoluminescence (TL) and persistent luminescence techniques. In the TL glow curve by UV charging at 100 K, two broad TL glow bands were observed around 160 and 390 K. The higher TL glow band was not observed by 550 nm charging at 300 K, but it was observed by charging at 400 K, which corresponds to the onset temperature of luminescence quenching. Because the 550 nm light excites the lowest $5d$ level of Eu^{2+} , we conclude that the luminescence quenching of $\text{CaAlSiN}_3\text{:Eu}^{2+}$ at high temperatures is caused by the thermal ionization.

1. Introduction

White LEDs (Light Emitting Diodes) illumination are rapidly replacing incandescent lamps and (compact) fluorescent tubes in the indoor lighting markets. This revolution in indoor lighting has been enabled not only by the invention of the blue LED¹, but also by the development of visible phosphors. The conventional white LED (w-LED) is a phosphor converted white-LED, which is composed of an InGaN-based blue LED and visible light emitting inorganic phosphors. From the dawn of the w-LED development, the w-LEDs usually use the $\text{Y}_3\text{Al}_5\text{O}_{12}\text{:Ce}^{3+}$ yellow phosphor^{2, 3}, but it does not show high color rendering due to the lack of red luminescent component. In 2006, Ueda, Hirosaki and Yamamoto developed a new red phosphor of $\text{CaAlSiN}_3\text{:Eu}^{2+}$, which has strong absorption at blue LED wavelength, high quantum efficiency and excellent thermal quenching behavior.^{4, 5} Since this discovery, the $\text{CaAlSiN}_3\text{:Eu}^{2+}$ phosphor has become one of the typical red phosphors for warm w-LEDs although many alternative phosphors have been designed.⁶

Especially, such an excellent thermal quenching behavior is important for the w-LED phosphors because the temperature of the LED chip reaches up to $\sim 200^\circ\text{C}$ in recent high power w-LED applications. However, even the $\text{CaAlSiN}_3\text{:Eu}^{2+}$ phosphor still shows thermal quenching at higher temperatures above 400 K⁷. For this thermal quenching mechanism, two possibilities have been considered. One is the thermally activated crossover from the $5d$ level to the $4f$ levels⁷⁻⁹, the other is the thermal ionization from the $5d$ excited level to the bottom

of the conduction band (CB).^{10, 11} Zhang and Hintzen et al. investigated the energy gap between the lowest $5d$ level of Eu^{2+} and Yb^{2+} and the bottom of CB ($\Delta E_{5d\text{-CB}}$) and found the correlation between thermal quenching behavior and $\Delta E_{5d\text{-CB}}$.¹² Thus, they proposed the thermal ionization quenching in $\text{CaAlSiN}_3\text{:Eu}^{2+}$ as well as $\text{CaAlSiN}_3\text{:Yb}^{2+}$. Also, because the thermal ionization quenching was predicted and proved in other Eu^{2+} phosphors by the investigation of energy diagram¹³⁻¹⁵ and photoconductivity^{16, 17}, the thermal ionization process may be the most probable path in the $\text{CaAlSiN}_3\text{:Eu}^{2+}$ phosphor.

In this study, the possibility of the thermal ionization process was investigated using thermoluminescence (TL) and persistent luminescence (PersL) spectroscopy. In general, TL as well as PersL is caused by detrapping of electrons, that were previously trapped, and by the recombination with hole-trapped luminescence center. Electron charging occurs when electrons in the excited state of luminescence centers are transferred to the CB (e.g., through thermal ionization) and then captured by traps in the host. Thus, the TL and PersL intensity depend on the thermal ionization efficiency in the non-saturation condition of electron traps. Recently, we successfully demonstrated the thermal ionization quenching of the most widely used $\text{Y}_3\text{Al}_5\text{O}_{12}\text{:Ce}^{3+}$ yellow phosphors by observation of the charging process from the lowest $5d$ level to the CB at high temperatures in the TL excitation spectrum¹⁸. For the $\text{CaAlSiN}_3\text{:Eu}^{2+}$, a broad TL glow band in the range between 300 to 673 K was reported¹⁹. Therefore, the investigation of thermal ionization quenching by TL and PersL measurements can be applied for the $\text{CaAlSiN}_3\text{:Eu}^{2+}$ phosphor.

2. Experimental

$\text{CaAlSiN}_3\text{:Eu}^{2+}$ (1%) phosphor was prepared by the solid-state reaction at 1800°C under N_2 gas of 10 atm. A crystalline phase was identified as a single phase of CaAlSiN_3 crystal. Temperature dependence of PL spectra was measured by a multichannel CCD spectrometer (QE65PRO, Ocean Optics,) and a cryostat (Helitran LT3, Advanced Research Systems). A combination of a 300-W Xe lamp (MAX-302, Asahi Spectra Co., Ltd) and a bandpass filter (460 nm) was used as the excitation source. TL glow curves were obtained using the cryostat and a photomultiplier tube (R3896, Hamamatsu Photonics, Hamamatsu). For the excitation source for the TL glow curve measurement, the Xe lamp with a UV cold mirror and with a 550 nm bandpass filter was used.

Photoluminescence excitation (PLE) and persistent luminescence excitation (PersLE) spectra were measured using a fluorescence spectrophotometer (RF-5000, Shimadzu). In

the persistent luminescence excitation measurement, the sample was charged by the monochromatic light for 1 min, and then a persistent spectrum was measured 1 min after ceasing excitation. The charging wavelength was changed by 10 nm intervals from 680 to 200 nm.

3. Results and Discussion

Figure 1 shows PL spectra of the $\text{CaAlSiN}_3:\text{Eu}^{2+}$ sample at different temperatures from 85 to 785 K. At all temperatures, a red luminescence band due to $\text{Eu}^{2+}:5d-4f$ was observed. With increasing temperature, the peak wavelength of PL band is shifted to shorter wavelength and the FWHM (full width at half maximum) becomes wider. This is because the Eu^{2+} ions with 5d excited state obey the Boltzmann distribution and the population of Eu^{2+} with higher 5d excited state coupled with several phonons increases with increasing temperature.

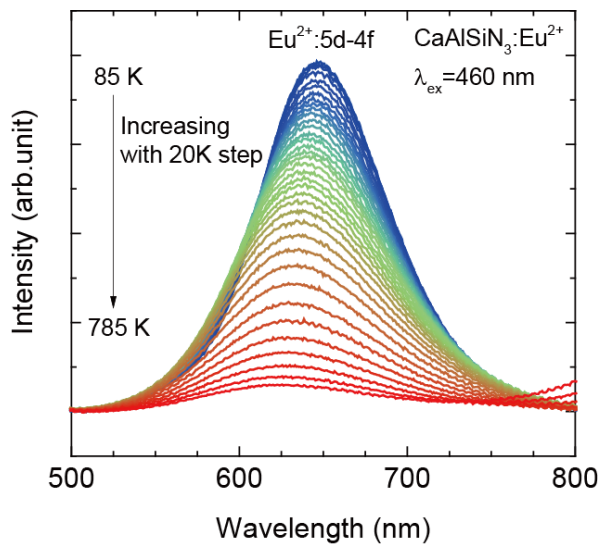


Figure 1. PL spectra of $\text{CaAlSiN}_3:\text{Eu}^{2+}$ by 460 nm excitation at different temperatures.

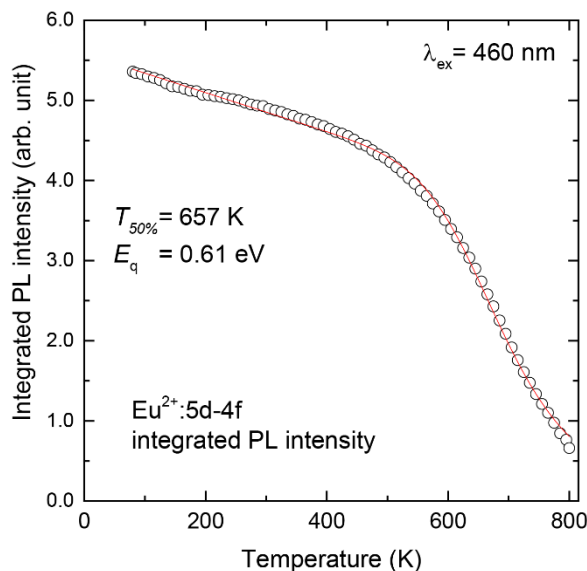


Figure 2. Temperature dependence of $\text{Eu}^{2+}:5d-4f$ PL intensity.

The temperature dependence of integrated PL intensity is shown in Figure 2. The PL intensity slightly decreases with a gentle slope up to 400 K and the slope changes to be steeper. The initial decrease of photoluminescence intensity can be caused by the temperature dependence of absorption coefficient

at 460 nm. Assuming linear decreasing dependence of absorption coefficient with increasing temperature, the temperature dependence of PL intensity can be fitted below equation,

$$I(T) = (I_0 - a \times T) / (1 + \Gamma_0/\Gamma_v \exp(-E_q/kT)) \quad (1).$$

Where, $I(T)$ is the PL intensity at a given point in temperatures, I_0 is the intensity at 0 K, Γ_v is the radiative rate, Γ_0 is the attempt rate of the nonradiative process, E_q is the activation energy for nonradiative process, k is the Boltzmann constant, T is the temperature and a is the factor of proportionality for temperature dependence of absorption coefficient. From the fitting result, the activation energy for main quenching process was estimated to be 0.61 eV, and Γ_0/Γ_v was 2.6×10^4 . To elucidate the main temperature quenching above 400 K, we tried to investigate the possibility of thermal ionization quenching by the thermoluminescence technique.

Figure 3 shows the luminescence decay curve of $5d-4f$ luminescence in the $\text{CaAlSiN}_3:\text{Eu}^{2+}$ sample. Typical fluorescence decay curve of the $\text{Eu}^{2+}:5d-4f$ transition was observed. The decay curve was fitted by below equation,

$$I(t) = I_0 \times \exp(-t/\tau) \quad (1).$$

Here, $I(t)$ is the PL intensity at a given point in time (t), I_0 is the initial intensity, τ is the lifetime. From the fitting result, the lifetime was estimated to be 801 ns. Because the thermal quenching is not caused at room temperature, the non-radiative rate is roughly regarded as 0. Thus, the radiative rate can be calculated to be approximately $1.3 \times 10^6 \text{ s}^{-1}$ from the reciprocal of the lifetime.

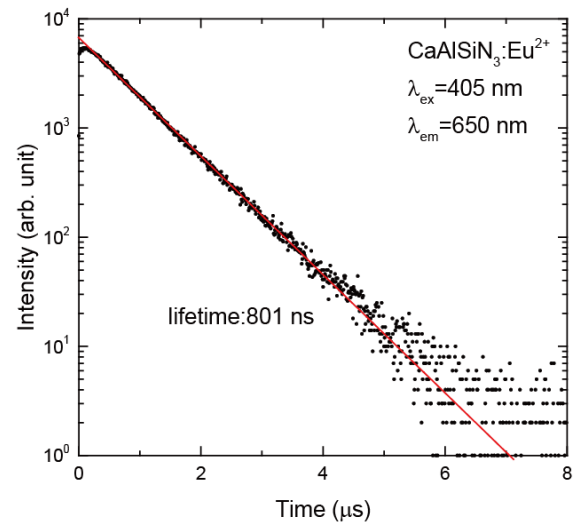


Figure 3. Fluorescence decay curve of $\text{CaAlSiN}_3:\text{Eu}^{2+}$.

Figure 4a shows the TL glow curves after UV charging at 80 K and 300 K and after 550 nm charging at 300 K. From the TL glow curve by UV charging at 80 K, two main TL glow bands were observed at 163 and 392 K. These two TL glow bands correspond to shallow and deep traps, which can be originated from some intrinsic or extrinsic defects. The most probable electron trap can be oxygen impurity in the N^{3-} site (O_N^{3-})¹⁹. Because the present sample shows a high TL glow band above 400 K which is the onset temperature of main thermal quenching, the quenching process by thermal ionization from the lowest 5d energy level to CB can be evaluated by the measurement of TL glow curves. In Figure 4a, the TL glow peak at around 392 K was also observed after UV charging at 300 K, but not observed after 550 nm excitation at 300 K. The 550 nm wavelength corresponds to the transition wavelength from the 4f ground to the lowest 5d level of Eu^{2+} in the CaAlSiN_3 host. Thus, the thermal ionization process from the lowest 5d level to the

conduction band does not occur at 300K. The thermal energy at 300 K is not large enough to overcome the energy barrier from the lowest $5d$ level to the CB. On the other hand, when the charging temperature increases from 300 K to 500 K by 50 K each, TL glow bands start to appear in the range between 400 K and 600 K even by 550 nm excitation as shown in Figure 4b. The observation of TL glow peak at higher charging temperatures shows that the charging process from the lowest $5d$ level to the CB is caused by the thermally activated process.

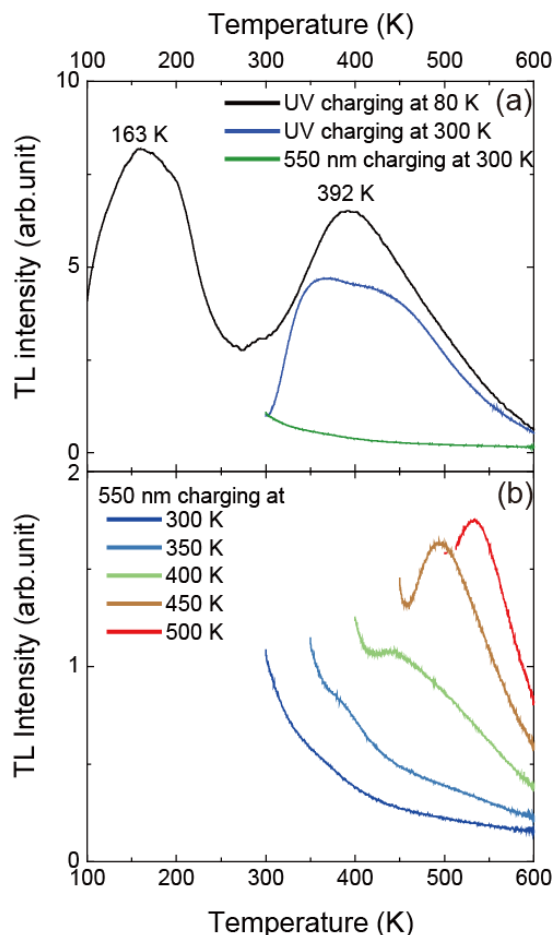


Figure 4. TL glow curves (a) by UV charging at 80K and 300K and by 550nm charging at 300K and (b) by 550nm charging at different temperatures.

In order to check the possibility of thermal ionization process from the lowest $5d$ levels in detail, the persistent luminescence excitation spectra were measured at 300 K and 450 K. Figure 5b and 5c show that the contour plots of persistent luminescence intensity versus charging wavelength and emission wavelength at 450 K and 300 K, respectively. The $\text{CaAlSiN}_3\text{:Eu}^{2+}$ sample exhibited red persistent luminescence at 300 K and 450 K after UV excitation. The generation of persistent luminescence can be understood from the broad TL glow curves in the range between 300 and 600 K as shown in Figure 4a. In the contour plot of PersL intensity at 300 K, the red persistent luminescence band was observed only after UV excitation from 250 nm to 350 nm, but not after visible excitation. On the other hand, in the contour plot at 450 K, a PersLE band from 350 nm to 650 nm was observed in addition to the UV PersLE band. From the PLE spectrum of 700 nm in $\text{CaAlSiN}_3\text{:Eu}^{2+}$ as shown in Figure 5a, the lowest $5d$ excitation band spreads from 500 to 650 nm. In the same range, the

PersLE band was also observed only in PersLE spectrum at 450 K, but not at 300 K. Based on these results, we conclude that the thermal quenching of $\text{CaAlSiN}_3\text{:Eu}^{2+}$ luminescence is caused by thermal ionization process, not by internal crossing quenching from $5d$ level to $4f$ level.

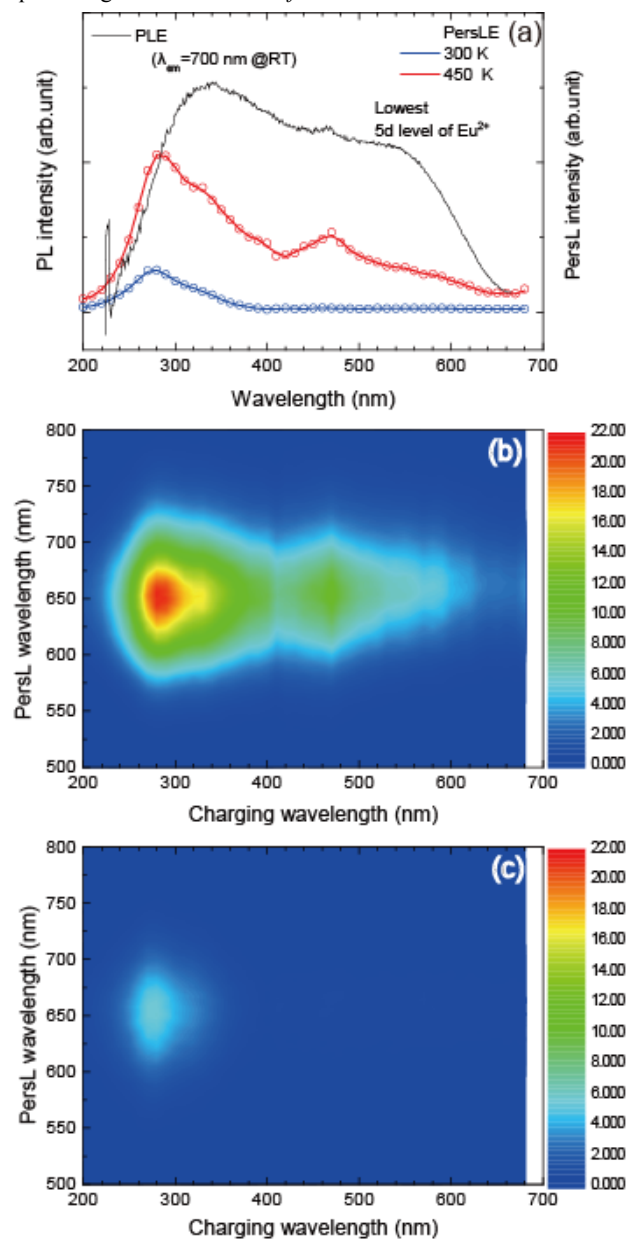


Figure 5. (a) Comparison of PLE and PersLE at 300 K and 450K. Contour plot of PersL intensity versus charging wavelength and PersL wavelength at (b) 450 K and (c) 300K.

This thermal ionization quenching is also understood from the vacuum referred binding energy (VRBE) diagram as shown in Figure 6. Lanthanide-host referred binding energy (HRBE) diagram in CaAlSiN_3 host was reported by Zhang, and Hintzen et al.²⁰ and the VRBE of Eu^{2+} was reported by Dorenbos²¹. Using these reported parameter such as host exciton energy ($E^{\text{ex}} = 4.9$ eV) at room temperature, charge transfer energy of Sm^{3+} ($E^{\text{CT}}_{\text{Sm}^{3+}} = 3.91$ eV), VRBE of Eu^{2+} in CaAlSiN_3 ($E_4(7,2+,\text{CaAlSiN}_3) = -3.71$ eV), the VRBE diagram was constructed as shown in Figure 6. Here, we assumed that the host exciton energy shifts to higher energy by approximately 0.15 eV from 300K to 10K. Also, to correct the electron and hole

binding energy, the host exciton energy at low temperature was multiplied by 1.08.²² As a result, the band gap was estimated to be 5.5 eV. From the VRBE diagram, the energy gap between 5d energy level and the bottom of CB (ΔE_{5d-CB}) is estimated to be 0.65 eV. The excited electron at the 5d level can be jumped to CB at higher temperatures because of this moderate energy gap between these. The VRBE diagram also supports the thermal ionization quenching in $\text{CaAlSiN}_3:\text{Eu}^{2+}$.

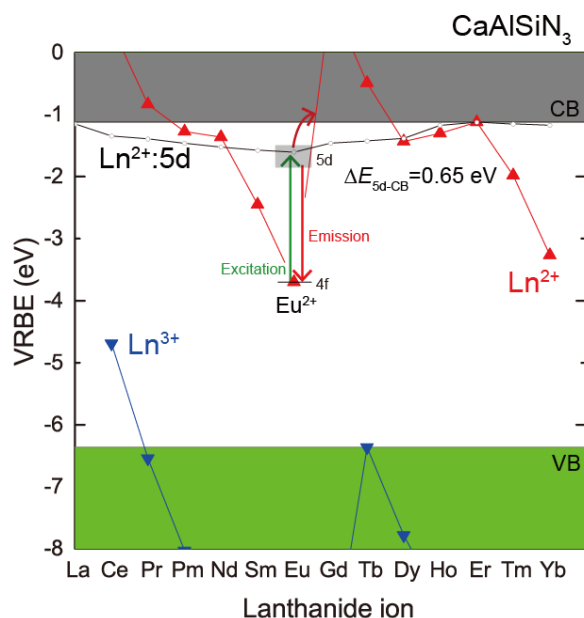


Figure 6. VRBE diagram of CaAlSiN_3 .

4. Conclusion

The photoluminescence spectra of $\text{CaAlSiN}_3:\text{Eu}^{2+}$ was measured at various temperatures from 80 K to 800 K. The PL intensity decreases with increasing temperature. In order to investigate the possibility of thermal ionization quenching, thermoluminescence (TL) and persistent luminescence excitation spectra were measured. In the TL glow curve by UV charging at 100 K, two broad TL glow bands were observed around 160 and 390 K. The higher TL glow band was not observed by 550 nm charging at 300 K, but it was observed by 550 nm charging at 400 K which corresponds to the onset temperature of luminescence quenching. Because the 550 nm light excites the lowest 5d level of Eu^{2+} , the charging process from the lowest 5d level is caused at high temperatures. In addition, the lowest 5d band of Eu^{2+} was observed in the persistent luminescence excitation spectrum at 450 K, while the 5d₁ excitation band was not observed at 300 K. These results show that the quenching process of the $\text{CaAlSiN}_3:\text{Eu}^{2+}$ phosphor is due to the thermal ionization. The moderate energy gap (0.65 eV) between the lowest 5d level and the conduction band in the vacuum referred binding energy diagram also supports the thermal ionization process.

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Graphical Abstract

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<Summary>

$\text{CaAlSiN}_3:\text{Eu}^{2+}$ shows thermal quenching from around 400 K. Based on the results of thermoluminescence glow curves and persistent luminescence excitation spectra, the electron charging process from the lowest 5d excited state of Eu^{2+} to conduction band was observed at 450 K. We conclude that the luminescence quenching of $\text{CaAlSiN}_3:\text{Eu}^{2+}$ at high temperatures is caused by the thermal ionization.

<Diagram>

